JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Article

pubs.acs.org/JAFC

Comparison of Simulated Pesticide Concentrations in Surface Drinking Water with Monitoring Data: Explanations for Observed Differences and Proposals for a New Regulatory Modeling Approach

Michael F. Winchell[†,*] and Nathan J. Snyder[‡]

[†]Stone Environmental, Inc., 535 Stone Cutters Way, Montpelier, Vermont 05602, United States

[‡]Waterborne Environmental, Inc., 897-B Harrison Street S.E., Leesburg, Virginia 20175, United States

ABSTRACT: A primary component to human health risk assessments required by the U.S. Environmental Protection Agency in the registration of pesticides is an estimation of concentrations in surface drinking water predicted by environmental models. The assumptions used in the current regulatory modeling approach are designed to be "conservative", resulting in higher predicted pesticide concentrations than would actually occur in the environment. This paper compiles previously reported modeling and monitoring comparisons and shows that current regulatory modeling methods result in predictions that universally exceed observed concentrations from the upper end of their distributions. In 50% of the modeling/monitoring comparisons, model predictions were more than 229 times greater than the observations, while, in 25% of the comparisons, model predictions were more than 4500 times greater than the observations. The causes for these overpredictions are identified, followed by suggestions for alternative modeling approaches that would result in predictions of pesticide concentrations closer to those observed.

KEYWORDS: *pesticide, modeling, monitoring, surface water, water supply*

INTRODUCTION

Regulation of agricultural pesticides use in the Unites States is required to be protective of both human health and the environment. The U.S. Environmental Protection Agency (EPA) assesses the risk of a particular pesticide use to human health from all nonoccupational sources by determining an estimated drinking water concentration (EDWC) of the pesticide, generally using simulation models, and combining this with other possible routes of exposure (food and residential sources) for comparison against human health effects metrics (the pesticide toxicity). Occupational exposure is assessed under a separate paradigm. The aggregate exposure is compared with effects data so that the risk manager may make an informed decision based on the risk characterization. The EDWC is often the determining factor in a risk assessment, and the accurate estimations of exposure are worthy of evaluation and improvements as technology and available data improve. EDWCs are calculated for both groundwater and surface water, with the higher of the two values representing the exposure level in the risk assessment. While challenges exist in the determination of groundwater and surface water EDWCs, this paper will focus on surface water. Surface water EDWCs can be determined from direct monitoring of raw and finished water in surface water supplies (for already registered products), modeling the pesticide fate and transport in surface drinking water using established regulatory tools or refined tools, or a combination of the two approaches. While extensive monitoring of pesticide residues in drinking water systems has occurred in the US over the past few decades, the need to calculate EDWCs for certain types of water systems and pesticides lacking more extensive monitoring records (especially limited and new use products) will continue. For this reason, modeling of pesticide EDWCs is the most common approach taken when conducting risk assessments; however, the usefulness of existing monitoring programs should not be ignored in their ability to validate the regulatory process and modeling predictions made by the EPA.

Current Regulatory Modeling Approach. In pesticide registration review, the U.S. EPA follows a tiered risk assessment process that applies more conservative aquatic exposure modeling methods for estimating pesticide EDWCs at the lower tiers and only applies more complex, refined modeling approaches for those pesticides that have not passed the risk assessment at the lower tiers. The Tier 1 modeling approach (designed to be most conservative) uses EPA's FIRST model,[1] and because most pesticides fail this initial tier, a Tier 2 assessment is often required. In a Tier 2 assessment, the EPA requires that a standard modeling approach utilizing the Pesticide Root Zone Model (PRZM) field scale hydrologic model[2] and the Exposure Analysis Modeling System (EXAMS) receiving water model[3] be followed when estimating pesticide EDWCs for the purpose of product registration. Refinements including Percent Crop Area (PCA) adjustments to the assumption of 100% cropping are within the Tier 2 guidance, but other refinements are limited. Registrants have at times submitted more complex modeling approaches that incorporate site specific environmental conditions (e.g., soil and weather), probabilistic methods (e.g., Monte Carlo simulation), specialized models, spatial analysis of model input parameters, and monitoring data as a Tier 3 and Tier 4 assessment to further refine exposure predictions.[4] US EPA acceptance of Tier 3 and

Received: August 25, 2013
Revised: December 12, 2013
Accepted: December 13, 2013
Published: December 13, 2013

dx.doi.org/10.1021/jf4036996 | J. Agric. Food Chem. 2014, 62, 348−359

Tier 4 has been limited, so in practice, exposure modeling beyond the screening level assessment provided in Tier 2 is rarely conducted, making the Tier 2 modeling results the most relevant for comparison with monitoring data.

The modeling results reported on in this study were generated using the Tier 2 modeling approaches that were prescribed by the EPA at the time the studies were conducted. The Tier 2 approach simulates daily concentrations of a pesticide in an "Index Reservoir" over a 30-year period. The Index Reservoir was characterized by the US EPA as being "designed to mimic drinking water reservoirs in the central Midwest known to be highly vulnerable to contamination from pesticides used in agriculture".[5] This Index Reservoir and its associated watershed is based on the Shipman Reservoir in Illinois. The Shipman Reservoir covers approximately 5.3 ha, has a mean depth of 2.7 m, and has a watershed that drains approximately 172.8 ha. These geometric characteristics result in a drainage area to normal capacity ratio (DA/NC) of 12, which is higher than approximately 90% of drinking water reservoirs.[5] Because higher DA/NC ratios lead to higher pesticide exposure vulnerability, the geometric characteristics of the Index Reservoir place it on the high end (90th percentile) of vulnerability.

The use of Shipman Reservoir to represent the Index Reservoir scenario for estimating EDWCs was designed to be conservative; therefore, the predicted pesticide concentrations are expected to be higher than would be found in most drinking water reservoirs.[6] Another important input assumption when applying the Index Reservoir scenario to calculate EDWCs is the percent cropped area (PCA) adjustment factor. A PCA adjustment factor is necessary because, for watersheds greater than a few hectares in size, the percentage of the watershed being cropped will be less than 100%. The PCA is a critical input assumption to the Index Reservoir modeling approach because it dictates the fraction of the reservoir watershed that will be treated with the pesticide under evaluation. The US EPA has recently developed updated guidance on how PCA adjustment factors should be determined for major crop and crop groups for both national and regional assessments.[7] This guidance provides recommendations of national and regional PCA values for major crops, for combinations of major crops, and for all agriculture, as well as a prescribed methodology for choosing the appropriate PCA value for a given pesticide use pattern scenario. While this recent guidance supersedes the approaches to PCA calculation that were effective at the time when several of the modeling studies in this report were conducted, the differences in PCA values between current and past guidance are small relative to the magnitude of the modeled versus monitoring data concentrations. Furthermore, the recommended PCA values in the most recent guidance are generally higher than the previously guidance, making the current model predictions more conservative than past analogous predictions. The national maximum PCAs for the major crops that were recommended for use during the period between 2000 and 2012[8] and the current post-2012 guidance are shown in Table 1.

The only legal constraints on pesticide use are the conditions for use placed on a product label. These conditions (for agricultural products, the application rates and timing on specific crops) are what EPA uses as a basis for modeling exposure, focusing on what could occur as opposed to what actually occurs or is likely to occur. Following the EPA modeling approach, the PCA and subsequently the fraction of the watershed treated with pesticide are constant for all pesticides that are labeled for use on a particular crop, regardless of the relative market share of individual products or the prevalence of actual use. Additionally, it is assumed that application of the pesticide is made over the entire cropped area in the watershed on the same day. The assumption that the entire cropped area is treated on the same day is likely to be more accurate for very small watersheds and low acreage crops consisting of a few fields under the management of few farmers, but it quickly becomes less realistic as the watershed size increases or for high acreage crops (due to farmer equipment constraints or pest and weed management strategies). Misrepresentation of actual product use spatially and temporally can have a significant impact on EDWCs. In order for models to successfully predict pesticide concentrations that can realistically be expected to occur under high vulnerability conditions, the product use assumptions must reflect reality. A comparison of modeling results with monitoring data will give an indication of model performance but also how well assumptions used for input values reflect actual conditions.

Table 1. Comparison of National Percent Cropped Area (PCA) Adjustment Factors for Major Crops from US EPA Guidance during 2000–2012 and Updated Guidance for 2012–Present

crop	max percent cropped area (2000–2012)	max percent cropped area (2012–current)
corn	0.46	0.61
soybeans	0.41	0.57
wheat	0.56	0.38
cotton	0.2	0.33
all agricultural land	0.87	0.91

Comparing Modeling to Monitoring Data. Making comparisons of water quality modeling results and monitoring data is a common activity used in model calibration and validation. Often times, these comparisons are not straightforward due to monitoring frequency and sampling methods relative to the modeling data.

One common comparison approach is to perform time series analysis where monitoring data and modeling results are evaluated over specific time periods (typically daily) where the two co-occur. A time series analysis can also occur based on longer duration time steps (monthly or annually) where both the monitoring and modeling data are aggregated over the duration being assessed. Obtaining an accurate assessment of model performance from time series analysis can be challenging in pesticide simulation modeling due to the uncertainties in pesticide application timing and subsequent transport to receiving waters. These uncertainties make the quantification of differences between model and monitoring data difficult, because the time series goodness of fit statistics are very sensitive to small timing errors in the model. The difficulty in applying time series comparison methods is even more difficult in situations where the number of monitoring samples is small compared to the number of model predictions. In situations where pesticide application timing is very well understood and monitoring data is more abundant, a time series analysis can be a meaningful approach for assessing the performance of pesticide concentration simulations. Another approach for comparing modeling and monitoring data is to perform statistical comparisons of the probability distributions of the two data sets. This type of approach places less emphasis on

assessing the model's ability to match temporal signals in the monitoring data and, instead, looks to assess the model's ability to predict concentration magnitude and frequency. This approach is particularly appropriate for pesticides where the specific temporal use patterns are often highly uncertain and where the monitoring data may not be able to capture the details of day to day temporal variability.

When making comparisons between modeling and monitoring data, the uncertainties inherent in both need to be considered. Uncertainties in modeling arise from the identification of model parameters, measured model inputs, and the underlying conceptual model and model structure. Uncertainties in model parameters have long been recognized in pesticide exposure modeling, and parameter space sampling techniques, such as Monte Carlo Analysis, Latin Hypercube Sampling, and Deterministic Equivalent Modeling Method (DEMM), have been used to address them.[9−12] Unfortunately, techniques such as Monte Carlo analysis often do not include errors and uncertainties in model inputs, such as weather and pesticide application timing, which can often be as or more important as many model parameters included in a probabilistic approach. Often times, model uncertainty is reduced by the refinement of model parameters accomplished through calibration with monitoring data.

Uncertainty in monitoring data used to calibrate and validate hydrologic and water quality models is also well acknowledged, and can lead to poor identification of model parameters. Efforts to quantify this uncertainty and development of tools to aid in the comparison of monitoring data with model data have been developed[13,14] and may be used to improve model calibration. Techniques for quantification of uncertainties associated with a conceptual model and model structure are not commonly applied to water quality models with a static form used in pesticide exposure modeling; however, the existence of these uncertainties should be acknowledged.

One of the greatest sources of uncertainty associated with monitoring data is the potential bias in the monitoring data resulting from low sampling frequency. Arguments can be made that infrequent sampling at regular intervals in a monitoring program can sometimes miss the peaks in concentration which are important in the determination of EDWCs for use in risk assessments. While this argument cannot be disputed, the question of the sampling frequency required to enable accurate prediction of the "true" distribution in concentration levels remains a topic of interest and continued investigation. Crawford[15] evaluated the sampling frequency required to accurately predict various exceedance probabilities of annual maximum concentrations. Crawford found that required sampling frequency was dependent upon watershed size and the exceedance probability being detected. For example, the median annual concentration in water bodies draining lager watersheds (e.g., 16,400 km^2) can be estimated sufficiently by sampling 7 times per year. For the 95th percentile annual concentrations (5% exceedance probability) on smaller watersheds (90−250 km^2), a sampling frequency of 10 times per month during the runoff season following pesticide applications was required. In addition, Mosquin et al.[16] presented an approach for estimating higher percentile (lower exceedance probability) pesticide concentrations in surface drinking water from monitoring data sets of various frequencies. In addition, they provided estimates of the number of samples required to derive confidence bounds for the upper percentiles of concentration distributions. For example, an effective sample size of 59−69 can provide the estimates for the 95th percentile concentrations with sufficient statistical confidence (e.g., 95%), and increasing the sample size to 212 reduces the relative standard error to 30% or below. Other recent work has sought to quantify the potential bias in the estimates of higher percentile pesticide concentrations based on nondaily monitoring data.[17,18] These studies have suggested that bias factors (defined as the 95th percentile of the ratios of a true concentration end point derived from daily monitoring data to the corresponding estimate from nondaily sampling) increase as monitoring frequency decreases and as the desired averaging interval decreases in duration (i.e., the bias factor increases if estimating maximum versus 14-day average). Chen et al.[18] found an average bias factor of 2.4 when using 7-day sampling interval data to estimate an annual peak value, and Hetrick[17] found bias factors averaging 1.79 for estimating peaks from 4-day sampling data or 8.35 when using 28-day sampling data. The development of bias factors for estimating higher percentile pesticide concentrations from monitoring data of various sampling frequencies provides an important basis for the comparisons between modeling results and monitoring data obtained from nondaily sampling studies. While the development of methods for using monitoring data in statistical estimation of higher percentile pesticide concentrations will continue, modeling tools will always be required when assessing EDWCs for newly registered crop protection products.

The question of if and by how much pesticide EDWCs derived from the standard regulatory modeling approach overestimate actual pesticide concentrations in drinking water has long been one of considerable interest. Several authors have published comparisons of modeling and monitoring data within the past ten years.[19−24] These studies (and others) have determined that the regulatory modeling based EDWCs consistently overpredict the concentrations of pesticides found in surface drinking water monitoring data sets. As was stated, the US EPA's modeling approach is understandably designed to be conservative; however, the magnitude of the gap between modeled and observed pesticide concentrations in surface drinking water should be fully understood so that the modeling results can be applied more appropriately in the context of better understood certainty/uncertainty of the modeled estimates. This paper brings together a collection of previously published comparisons between monitoring data and regulatory modeling-based EDWCs, with the objective of evaluating how accurately the regulatory modeling approach being used by the U.S. EPA reflects what has been observed in monitoring studies. In combining data from multiple past studies, the analysis contained in this paper is based on the most comprehensive set of data on the subject to date. A secondary objective of this paper is to identify the possible factors leading to the overprediction of EDWCs following the current modeling approach and to propose alternative assumptions and methods that produce results closer to observed values of pesticide concentrations in surface drinking water.

MATERIALS AND METHODS

This comparison of modeling and monitoring data of pesticide concentrations focused on modeled EDWCs derived from standard US EPA Tier 2 regulatory modeling and monitoring data covering a wide range of water body types (flowing and nonflowing) and sizes. A preliminary literature review on the subjects of pesticide modeling and monitoring identified 179 documents from peer reviewed journal

articles, technical reports, conference proceedings and presentations, and Web sites. This initial bibliography was then screened to identify the studies that contained explicit comparisons between Tier 2 PRZM/EXAMS modeling results and monitoring data. This screening resulted in seven studies from which the data for evaluation were compiled. All the monitoring and modeling results reported in each of the seven studies selected were designed to select either the maximum or a higher percentile monitoring data concentration for comparison with the modeled values (which were generally the 1 in 10 year annual maximum values used in regulatory risk assessments). The discussion that follows and footnotes to the individual data tables will provide the information concerning each of the data sources and describe the methodology for the modeling/monitoring data comparisons made in this report.

Data Sources. The data sets, and descriptions of the source studies they came from, are provided in this section. First was the paper by Jones.[19] This study reported on four pesticides that were part of targeted monitoring studies that sought to identify community drinking water systems (CWS) that were in locations most vulnerable to potential exposure to each individual pesticide. The study included between 5 and 28 CWS for each pesticide, with between 233 and 2120 samples of raw water and between 30 and 306 samples of finished water (total samples per pesticide ranging from 263 to 2426). The sampling associated with these studies lasted between 2 and 3 years and included weekly or biweekly sampling frequency during and after the application season. The study compared both daily maximum concentrations and annual average concentrations. A summary of the data compiled from this study is provided in Table 2. In Table 2, the highest modeled concentrations represent the highest daily maximum value based on 30-year simulations of all multiple crop scenarios simulated for the pesticide shown. The highest monitoring concentration represents the highest of finished water over the duration of the study (2 to 3 years).

Table 2. Summary of Modeling and Monitoring Data from Jones[17]

pesticide	highest modeled conc[e] (μg/L)	max monitoring conc (μg/L)	EDWC duration	tot samples[f]
aldicarb[a]	17	0.68	acute (daily max)	2426
bromoxynil[b]	11	0.38	acute (daily max)	543
carbaryl[c]	745	0.16	acute (daily max)	2369
ethoprophos[d]	127	0.012	acute (daily max)	263
aldicarb[a]	5.8	0.07	chronic (annual avg)	2426
bromoxynil[b]	0.2	0.01	chronic (annual avg)	543
carbaryl[c]	31	0.005	chronic (annual avg)	2369
ethoprophos[d]	13	<0.003	chronic (annual avg)	263

[a]Includes 28 sites monitored for 3 years with weekly sampling during application season. [b]Includes 16 sites monitored for 2 years with biweekly sampling during application season. [c]Includes 20 sites monitored for 3 years with weekly sampling during application season. [d]Includes 5 sites monitored for 3 years with weekly sampling during application season. [e]Modeling conducted by EPA and represents 90th percentile annual maximum; for bromoxynil, value represents the average of annual maxima. [f]Raw water plus finished water samples.

The second source of data by Jackson et al.[20] examined 25 different pesticides, making predictions of EDWCs following the standard EPA PRZM/EXAMS regulatory modeling approach and comparing those results with monitoring data collected in the study of water supply reservoirs conducted by the US Geological Survey (USGS) and the US EPA.[25] The USGS study monitored 12 reservoirs over a period of one to two years (1999–2000) extending geographically across 12 different states, from California to New York . The reservoirs selected focused on small reservoirs with high pesticide use, and were thus highly vulnerable to elevated pesticide concentrations. A sampling strategy was designed to be able to estimate higher percentile (90th, 95th, and 99th percentile) with high confidence. The strategy was derived from an evaluation of a 2-year record of daily pesticide concentrations from Perry Lake reservoir in Kansas, and PRZM/EXAMS simulations. Three different sampling schemes were developed (11, 26, and 37 times per year), each of which focused samples during the pesticide application season. One of the 12 reservoirs received the highest sampling frequency (37 times per year), four reservoirs received the middle frequency (26 times per year), and seven received the lower frequency sampling, resulting in 537 to 551 samples per pesticide. In addition to data from the 2-year reservoir monitoring study, Jackson et al.[20] also presented monitoring data from the USGS National Water Quality Assessment (NAWQA) program as an additional data set for comparison. The NAWQA data set analysis included a longer record of water quality sampling (1992–2004) and a larger total number of samples for each pesticide, ranging from 105 to 23,726. The NAWQA sampling locations are not specifically targeted as sites having a high vulnerability to pesticide exposure, but rather represent a cross section of agricultural, developed, and mixed land use watersheds spread geographically across the United States. Sampling for NAWQA is generally conducted on a biweekly basis. One of the primary objectives of the NAQWA program is to monitor trends in surface water quality. A summary of the PRZM/EXAMS modeling and the monitoring results from the USGS reservoir monitoring and the NAWQA database analysis is provided in Table 3. The highest modeling concentration reported is the highest 90th percentile annual maximum concentration (from the 30-year PRZM/EXAMS simulations) simulated from one or more crop scenarios. The 90th percentile annual maximum concentrations are calculated by first determining the maximum concentration in each simulation year and then ranking those annual maximum concentrations and calculating the 90th percentile of those values. The data presented for the reservoir monitoring program represents the maximum concentration detected, while the data from the NAWQA program is the 95th percentile of the collection of samples. Although these two monitoring data sets are not equivalent, the additional NAWQA data provide a valuable comparison with both the modeled concentrations and the reservoir data.

A conference presentation by Hertl et al.[21] also compared modeling results following the EPA PRZM/EXAMS regulatory modeling approach with monitoring data from the USGS reservoir monitoring program.[19] This study evaluated several pesticides in addition to the Jackson et al.[20] study and also looked at both acute (short-term) and chronic (long-term) concentrations. The acute concentrations were represented by the maximum individual sample values, and the chronic concentrations were calculated as the 95th percentile of the time weighted annual average. In addition, the monitoring data evaluated in the Hertl et al.[21] study represented only the raw water samples, whereas the Jackson et al. paper included finished water as well, with a total number of samples per pesticide ranging from 312 to 323. For the vast majority of the pesticides analyzed, the raw water samples had higher concentrations than the finished water samples (highlighting another area of conservatism in the regulatory approach). These data are summarized in Table 4.

The most recent report reviewed that compared monitoring data to regulatory model simulation results was prepared by the US EPA.[7] The purpose of this report was to present an updated methodology for selecting appropriate PCA adjustment factors based on analysis of the most recent land use and cropping data sets. In addition to presenting the updated methodology, the report also showed monitoring data comparisons of the regulatory modeling simulations using the new PCA adjustment factors. In addition, the report included monitoring data from multiple sources (some were the same as those used in the earlier studies described) compiled over the past 20 years. These monitoring data sets included the following: USGS monitoring data from community water systems presented in *Concentration Data for*

Table 3. Summary of Modeling and Monitoring Data from Jackson et al.[16]

pesticide	highest modeled conc[a] (μg/L)	USGS reservoir program, max monitoring conc (μg/L)[b,c]	tot samples[f]	USGS NAWQA program, 95th percentile monitoring conc (μg/L)[e]	no. of NAWQA samples
2,4-D	145	0.634	537	0.362	7,129
2,4-DB	140	0.054	537	<0.24	5,938
acifluorfen	13.4	0.062	537	<0.035	6,014
aldicarb	98.7	0.082[d]	537	<0.55	5,980
atrazine(H)	438	11.6	551	1.4	23,726
benomyl	9.34	0.215	537	0.024	1,182
bentazon	32.5	0.344	537	0.1	6,488
bromoxynil	88.3	0.057	537	<0.035	5,877
clopyralid	15.8	0.17	537	<0.23	5,976
dicamba	32.5	0.192	537	<0.035	6,043
flumetsulam	2.25	0.088	537	<0.11	1,084
imazaquin	3.09	0.351	537	0.058	1,214
imazethapyr	3.06	0.133	537	0.028	1,128
linuron	35	0.035	537	<0.08	259
MCPA	81	0.121	537	<0.07	6,218
metalaxyl	101	0.351	538	0.04	656
methomyl	16.3	0.077[d]	537	<0.017	105
nicosulfuron	1.92	0.139	537	<0.013	1,089
norflurazon	215	0.414	537	<0.042	6,101
oryzalin	161	0.127	537	<0.31	6,056
picloram(H)	5.27	1.441	537	<0.05	5,763
propiconazole	125	0.064	537	<0.021	1,112
sulfometuron-methyl	1.87	0.16	537	0.025	1,165
tebuthiuron	1350	0.077	537	0.049	14,133
terbacil	125	0.1	537	<0.034	10,223

[a]Modeled values represent 90th percentile of annual maxima. [b]Data presented in Jackson et al. (2005) was graphical. Specific values reported were extracted directly from Bloomquist et al. (2001). [c]Includes 12 sites monitored for 1 to 2 years with 11 to 37 samples per year, focused during application season (up to every 3 days for 1 month). [d]No detections occurred in sampling. Value represents detection limit. [e]Values preceded by "<" were below the level of quantification for the analytical method. [f]Raw water plus finished water samples.

Anthropogenic Organic Compounds in Ground Water, Surface Water, and Finished Water of Selected Community Water Systems in the United States, 2002–05 (http://pubs.usgs.gov/ds/2007/268/); USGS NAWQA surface water data (http://infotrek.er.usgs.gov/nawqa_queries/); the USDA's Pesticide Data Program (PDP); the California Department of Pesticide Regulation's Surface Water database (http://www.cdpr.ca.gov/docs/emon/surfwtr/surfdata.htm); and data obtained from crop-specific monitoring studies submitted to EPA. The comparisons in Echeverria et al.[7] represent the most current implementation of EPA's regulatory modeling approach as well as the most comprehensive compilation of monitoring data comparison. These data comparisons from the EPA report are summarized in Table 5. The highest modeling concentration shown represents the 1 in 10 year peak, or 90th percentile annual maximum concentration (see footnote earlier in this section). The total number of samples per pesticide was not provided in the EPA report; however, given that NAWQA was one of the sources, the number of samples likely well exceeded 1000 for many of the pesticides.

The four studies presented thus far accounted for the majority of the modeling results monitoring data comparisons. Three other studies provided additional comparisons of regulatory modeling results with monitoring data. The first study focused on the fungicide vinclozolin and its use on golf courses.[22] In this study, 10 CWS watersheds with high numbers of golf courses were monitored for over a two year period for vinclozolin. The second study assessed the herbicide oxadiazon, which is also used on turf.[23] In this study, three community water systems were monitored for a period of three years. The third study was an analysis of fungicide iprodione use on turf and included its degradate product, 3,5-DCA.[24] This study compared monitoring data of finished water collected over three years from three different CWS with regulatory modeling predictions. The modeling and monitoring data from these three studies, including the total number of monitoring samples (ranging from 480 to 639), are presented in Table 6.

Data Compilation and Analysis. The modeling/monitoring data comparison from the seven studies presented in Tables 2–6 were combined for an assessment of the modeled data overprediction in surface water EDWCs. For the Jackson et al.[20] study, only the monitoring data from the USGS reservoir study was included for the combined comparison. This was done because, for all pesticides, the monitoring data from the USGS reservoir monitoring found greater concentrations than the 95th percentile data from the NAWQA analysis. There were a total of 85 modeling/monitoring data points for evaluation. These 85 data points included 68 acute and 17 chronic EDWC concentrations spread over 52 different pesticides (52 acute and 15 chronic). The overprediction in the modeled concentration was calculated as the ratio of modeled concentration to monitored concentration. The results of this analysis follow.

RESULTS AND DISCUSSION

Analysis of Modeling and Monitoring Data Comparisons. All monitoring and modeling data comparisons from the seven studies compiled are shown in Figure 1a. The 85 data points are sorted from highest modeled concentration to lowest modeled concentration. Figure 1b shows only the 25 data points with the lowest modeled concentrations. The modeled concentrations ranged from a high value of 1350 μg/L (for tebuthiuron acute concentration) to a low value of 0.2 μg/L (for bromoxynil chronic concentration). The median modeled concentration was 32.5 μg/L (for bentazon, acute concentration), which had an associated monitoring concentration 2 orders of magnitude lower at 0.344 μg/L. In total, 96.5% of the

Table 4. Summary of Modeling and Monitoring Data from Hertl et al.[20]

pesticide	highest modeled conc[a] (μg/L)	max monitoring conc[b,c,d] (μg/L)	EDWC duration	tot samples[e]
acifluorfen	14.03	0.062	acute (daily max)	312
aldicarb	17.4	0.082	acute (daily max)	312
atrazine	205.1	11.6	acute (daily max)	323
azinphos-methyl	87.8	0.144	acute (daily max)	323
carbaryl	274	0.063	acute (daily max)	323
disulfoton	26.8	0.021	acute (daily max)	323
fenamiphos	651	0.016	acute (daily max)	317
metolachlor	134.6	3.32	acute (daily max)	323
triallate	7.76	0.002	acute (daily max)	323
tribuphos	14	0.016	acute (daily max)	317
acifluorfen	2.97	0.062	chronic (annual avg)	312
aldicarb	5.8	0.082	chronic (annual avg)	312
atrazine	194.2	2.016	chronic (annual avg)	323
azinphos-methyl	7.2	0.018	chronic (annual avg)	323
carbaryl	79	0.063	chronic (annual avg)	323
disulfoton	1.1	0.017	chronic (annual avg)	323
fenamiphos	329	0.016	chronic (annual avg)	317
metolachlor	77.9	0.417	chronic (annual avg)	323
triallate	0.88	0.001	chronic (annual avg)	323
tribuphos	2	0.016	chronic (annual avg)	317

[a]Modeling conducted by EPA and Represents 90th percentile annual maximum. [b]For nondetections, where the 95th percentile could not be determined (chronic), the detection limit was used. [c]Includes 12 sites monitored for 1 to 2 years with 11 to 37 samples per year, focused during application season (up to every 3 days for 1 month). [d]Acute represents the maximum detected, and chronic represents the 95th percentile of the time-weighted average. [e]Raw water samples.

modeled concentrations were greater than 1 μg/L, while the monitoring data values were greater than 1 μg/L only 10.6% of the time. In all 85 comparisons, the monitoring data were lower than the modeling data.

The magnitude of the overprediction by the modeling results was quantified by calculating the ratio of the modeling concentration to the monitoring concentration. These ratios are plotted from low to high in Figure 2 using percentiles calculated from the Weibull plotting position. In addition, the 85 data points were split into acute and chronic comparisons. Based on the population of all 85 data points, the range in overprediction is from 1.5 to 85,041, with the median overprediction greater than 2 orders of magnitude (229×). More than 90% of the comparisons had a model overprediction of greater than 1 order of magnitude (10×). For one-third of all

Table 5. Summary of Modeling and Monitoring Data from Echeverria et al.[5]

pesticide	highest modeled conc[b] (μg/L)	max monit conc[b] (μg/L)	EDWC duration
acetochlor	50.1	4.77	acute (daily max)
acifluoren	49.5	0.011	acute (daily max)
atrazine	130.3	85	acute (daily max)
bentazon	11.7	0.12	acute (daily max)
bromacil	62.7	0.0927	acute (daily max)
bromoxynil	2	0.0046	acute (daily max)
carbofuran	25.2	0.0141	acute (daily max)
chlorthalonil	328.5	0.71	acute (daily max)
chlorthalonil	75.9	0.71	acute (daily max)
cycloate	44.4	0.6	acute (daily max)
cypermethrin	1.9	0.246	acute (daily max)
dcpa	416.7	0.0049	acute (daily max)
diazinon	135.8	0.0855	acute (daily max)
dicrotovos	16.6	6.83	acute (daily max)
fipronil	0.5	0.0375	acute (daily max)
fluometuron	29.7	0.0065	acute (daily max)
imazaquin	11	0.16	acute (daily max)
iprodione	163.2	0.018	acute (daily max)
linuron	17.7	5.28	acute (daily max)
mcpa	15.3	0.47	acute (daily max)
oryzalin	61.1	0.065	acute (daily max)
phosmet	2.6	0.074	acute (daily max)
picloram	8.6	0.17	acute (daily max)
triallate	3.3	0.65	acute (daily max)
triclopyr	516.6	0.45	acute (daily max)

[A]Modeled values represent 90th percentile of annual maxima. [b]Value represents maxima from multiple sources over many sites and many years. Refer to source report for details. [c]Total number of samples was not reported in source.

Table 6. Summary of Modeling and Monitoring Data from Jackson et al.,[21] Nandihalli et al.,[18] and Jones[22]

pesticide[a]	highest modeled conc[d] (μg/L)	max monit conc (μg/L)	EDWC duration	tot samples[e]
3,5-DCA[b]	153	<0.032	acute (daily max)	587
iprodione[b]	361	0.6	acute (daily max)	587
oxadiazon[b]	52	0.175	acute (daily max)	639
vinclozolin[c]	84.3	0.025	acute (daily max)	480
3,5-DCA[b]	36	<0.025	chronic (annual avg)	587
iprodione[b]	1.6	0.037	chronic (annual avg)	587
oxadiazon[b]	18.6	0.025	chronic (annual avg)	639

[a]Vinclozolin data from Jackson et al. (2010); oxadiazon data from Nandihalli et al. (2010); iprodione and 3,5-DCA data from Jones (2012). [b]Includes 3 sites monitored for 3 years with weekly/biweekly sampling. [c]Includes 10 sites monitored for 3 years with biweekly sampling for first 6 months, then monthly. [d]Modeled values represent 90th percentile of annual maxima. [e]Raw water plus finished water samples.

comparisons, the overprediction by the modeling results was greater than 1000×. When comparing the distribution of model overprediction for acute versus chronic EDWCs, the distributions are very similar between from the 30th through 90th percentiles. Below the 30th percentile, the chronic EDWC overpredictions are somewhat higher than the acute overpredictions. The smallest overprediction in the chronic EDWCs

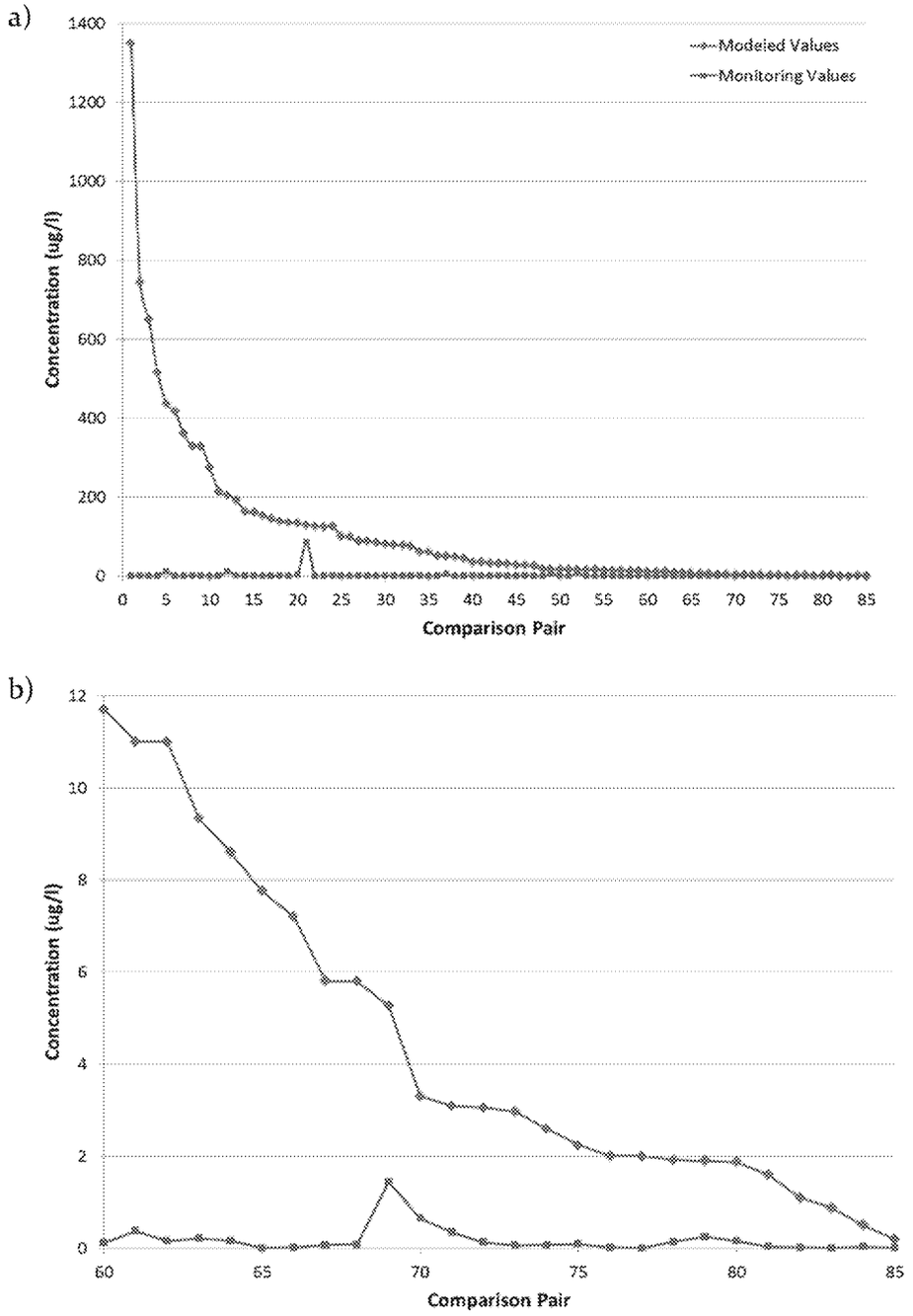

Figure 1. (a) Comparison of modeled and monitoring data concentrations for all pesticides, all data points. (b) Comparison of modeled and monitoring data concentrations for all pesticides, low concentration data points.

was 20× while the smallest acute overprediction was 1.16×. This suggests that, even as the regulatory modeling approach results in peak concentrations that are too high, the persistence of elevated concentrations that it predicts can lead to more significant overprediction of longer duration concentrations. This persistence of high concentrations may be in part due to the underestimation of inflows and outflows associated with the index reservoir assumptions.

The overprediction ratios by pesticide for the acute EDWC comparisons are shown in Figure 3. The average (arithmetic mean) was calculated for those pesticides (e.g., atrazine) where multiple comparisons of modeling and monitoring data were available. In the figure, (I) indicates an insecticide, (H) indicates a herbicide, (F) indicates a fungicide, (F,D) indicates a fungicide degradate, and (N) represents a nematocide. Based on the data in Figure 3, there are a few trends to note. First, three of the pesticides in the top ten highest overprediction ratios were fungicides or associated degradates, while no fungicides occurred among the lowest ten ratios. In addition, two of the pesticides in the top ten lowest overprediction ratios (acetochlor and atrazine) are among the top 5 highest use pesticides in the US in 2007.[26] Of the ten pesticides with the highest overprediction ratios shown in Figure 3, none of them were among the 25 pesticides with the highest use in the US in 2007. While the data available concerning actual pesticides use associated with each modeling/monitoring data comparison are limited at best, the comparison trend demonstrates a

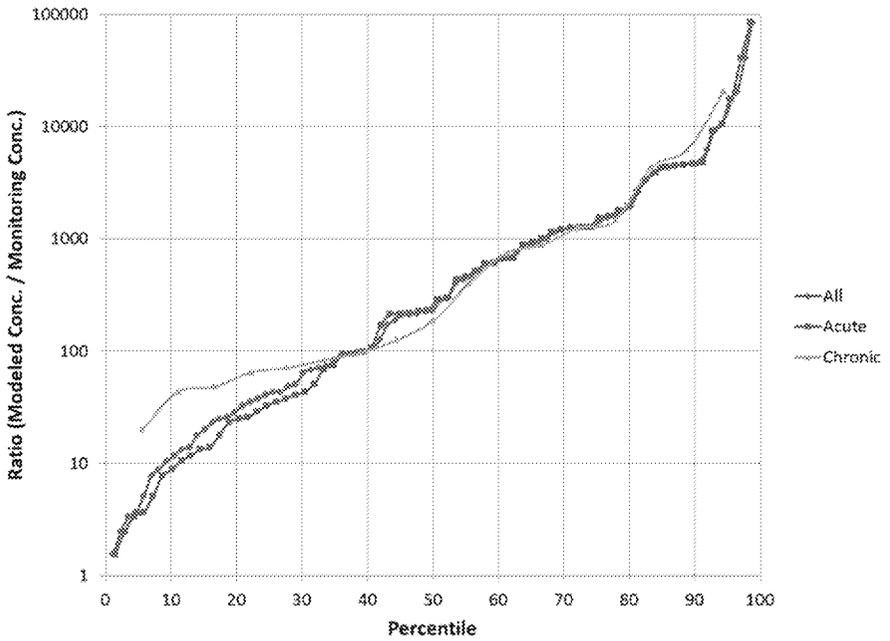

Figure 2. Overprediction ratios of EDWCs for acute, chronic, and all predictions pooled together.

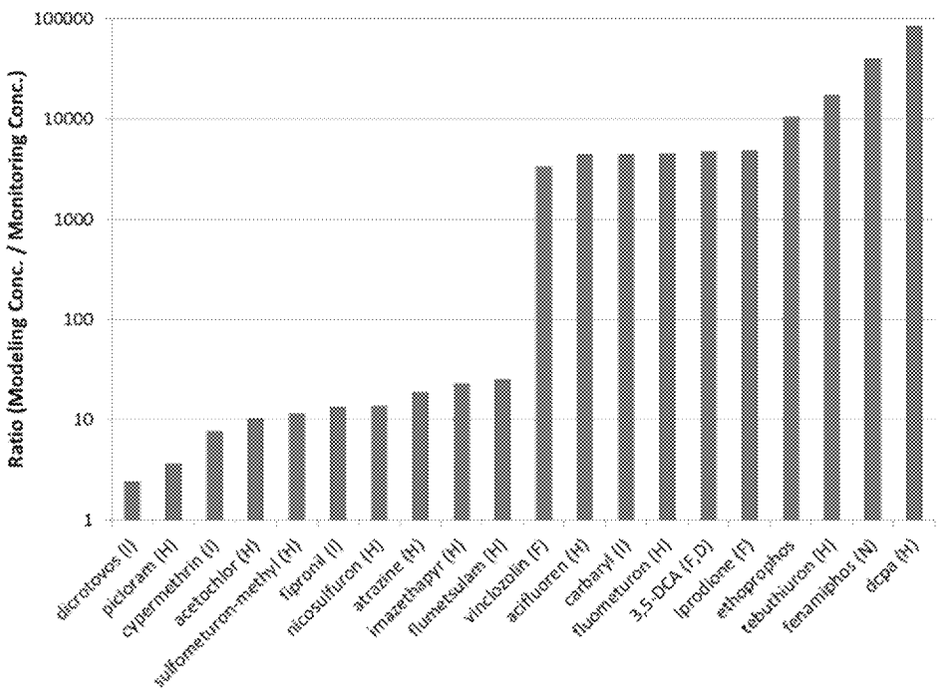

Figure 3. Top 10 and bottom 10 acute overprediction ratios of EDWCs by pesticide.

correlation between lower use pesticides and higher overprediction ratios.

Factors Affecting Model Comparisons with Monitoring Data. It must be acknowledged that the comparisons between the modeled EDWCs and monitoring data are not, and cannot be, absolutely equivalent comparisons, as the regulatory modeling was not conducted on a site-specific basis under monitoring watershed conditions (e.g., specific weather or soil characteristics). They were run under the generic Index Reservoir standard setting. One aspect of the monitoring data sets that is different than the modeling data is the sampling interval. The modeling data EDWCs are based on daily predictions, whereas the monitoring data sets are based on different prescribed sampling intervals. As has been discussed, the data sets cited in this paper all had annual sampling frequency in the range of once every 3-days to biweekly samples during the high runoff season. Although these nondaily sampling frequencies might have missed the true maximum concentration in a particular year, the annual mean (chronic end point) and/or the 90th percentiles (acute) concentrations over the many sites and years (up to 20 years) should provide sufficient statistical power for estimating these end points based on Crawford[15] and Mosquin et al.[16] Recall that Crawford[15] found that seven samples per year was sufficient to estimate median annual concentrations for larger watersheds, and 95th percentile annual maximum concentrations could be con-

dx.doi.org/10.1021/jf4036996 | J. Agric. Food Chem. 2014, 62, 348−359

fidently estimated with ten samples per month (every three days) during the runoff season. The sampling frequency in the monitoring studies contained in this report all exceeded the frequency required for estimates of annual mean concentrations (chronic), and several met or approached the frequency required to estimate the 95th percentile annual concentration (a level requiring more frequent sampling than the standard 90th percentile annual acute concentration). In addition, research concerning the bias factors between the true peak concentrations and peak concentrations[17,18] inferred from a nondaily sampling scheme indicated a weekly based sampling scheme could likely underestimate peak concentrations by a factor of 2.4 on average, whereas a 28-day sampling scheme could underestimate peak concentrations by a factor of 8.35 on average. The monitoring programs evaluated in the comparisons contained in this study included targeted monitoring (designed to sample high vulnerability sites), with weekly or sometimes more frequent sampling (sampling information is provided as footnotes associated with each data table and earlier in the text). A monitoring bias factor of around 3x is very small compared to the median model overprediction of 280x reported in the studies evaluated here.

A second aspect of the modeling data that differs from the monitoring data is the length of the model simulation compared to the monitoring sampling period. Model simulations for Tier 2 regulatory modeling are run for 30 years in order to account for climate variability. Although some of the monitoring data sets included in this study included longer periods of record (>10 years), such as some sources included in Echeverria et al.,[7] many were based on durations of two to three years.[19−24] If these monitoring studies were each considering only a single site, one might conclude that the shorter duration of the monitoring data would be expected to show potentially lower peak pesticide concentrations compared to a model simulation representative of a 30-year weather time series (with greater extremes). In the case of the studies presented in this report, this conclusion would not be valid, because all of the studies evaluated multiple sites throughout the monitoring period, effectively multiplying the number of sample years by the number of sites. For example, in the Jones study,[19] individual pesticide monitoring ranged from five sites for three years (15 effective site-years) to 28 sites for three years (56 effective site-years). The USGS targeted reservoir monitoring program,[25] which was used in model comparisons in several studies,[20,21] intensively monitored 12 sites for two years (24 effective site-years). By including multiple sites monitoring for the same pesticide, the potential for a low bias in the monitoring data due to having less climate variability than a 30-year modeling period is likely to be low. This can also be supported by the statistical work of Crawford[15] and Mosquin et al.,[16] who have shown that nondaily sampling data sets over many sites and years (up to 20 years in our cited data) should provide sufficient statistical power for estimating the annual mean (chronic end point) and/or the 90th (acute) concentrations. Recall that Mosquin et al.[16] found that an effective sample size of 212 is sufficient to estimate the 95th percentile concentrations with a relative error of 30% or less for a target population of monitoring. As can be seen in reviewing Tables 2−6, the total number of samples per pesticide used to compare with model results ranged from a minimum of 263 samples for ethoprophos (Table 2) to 23,736 samples in the case of the NAWQA atrazine data (Table 3), with most pesticides having greater than 500 samples. These findings suggest that the sample sizes in the monitoring data sets evaluated in this study are large enough to allow meaningful estimation of both chronic (annual mean) and acute (90th percentile) concentrations.

Framework for More Accurate Modeling of Drinking Water Exposures. This study included comparisons of modeling results generated by using standard EPA regulatory practices with monitoring data dating back to 2002,[21] continuing up through a comprehensive assessment compiled by the US EPA using that latest parametrization methodology.[7] Each of these studies concludes that, to varying degrees, the regulatory modeling approach overpredicts drinking water EDWCs. While overprediction by the modeling approach is consistent with the regulatory objective of protecting human health, the degree of overprediction identified in this study (median of nearly 280×) suggests that for most pesticides the current modeling approach may have unrealistically predicted a higher potential health risk than actually exists. Evaluation of the current modeling approach is thus warranted, including a critical review of the inputs and assumptions in the current approach that are responsible for the significant overprediction of EDWCs.

Many of the assumptions leading to the large overpredictions have been identified by the authors of previous publications on the subject. Hertl et al.[21] mention several factors leading to the overprediction, foremost among them being the overrepresentation of pesticide use in the Index Reservoir watershed. Even though a PCA adjustment factor is applied to lower the effective fraction of the Index Reservoir watershed receiving pesticide application, this PCA is based on a conservative estimate of crop extent and does not take into consideration information on actual pesticide use. The assumption that 100% of a given crop is applied across the whole watershed with the same pesticide under consideration at the maximum labeled rate (as is the assumption in regulatory modeling) is never true in reality, and for many pesticides with small market share, it is a gross overestimate of actual use. Hertl et al.[21] goes on to mention issues associated with the appropriateness of the PRZM/EXAMS model scale compared to the scale it is being used to simulate. PRZM is a single field model which is being used to simulate the hydrochemical behavior of a heterogeneous watershed. The PRZM model cannot account for watershed scale attenuation and the effects of interaction between adjacent landscape units (such as vegetated and/or riparian buffers) which have been shown to significantly reduce off-field transport of pesticides.[27] Furthermore, the issue of scale is a key factor in the assumptions of pesticide spray drift contributions to EDWCs in the index reservoir modeling scenario, which assumes that all treated fields are adjacent to water bodies contributing to the reservoir and that those water bodies are always downwind of the field treated with pesticide; an assumption that is physically an impossibility. Other factors contributing to the regulatory modeling overprediction include the compounding of conservative assumptions such as the following: selection of only a single representative but runoff vulnerable soil and the interpretation of product labels assuming the maximum rates at the minimum intervals to all fields within a watershed on the same day. The chemical specific environmental fate parameters chosen as inputs to the models are selected with each parameter individually representing the upper 90th of sample values for that parameter's data set. Collectively, however, combining these parameter values creates a vulnerability scenario much higher

than the 90th. Other authors[19,20] have identified similar factors contributing to regulatory model overprediction, with Jackson et al.[20] proposing a correction factor based on the total pesticide applied in the model simulation.

The authors of this paper support the suggestions by previous authors on the subject regarding the causes for overprediction in the regulatory modeling approach that are most responsible for model overprediction. There are several other factors that deserve mentioning and reinforcement. First, as stated in the Introduction, the Index Reservoir scenario is based on CWS with a very low drainage area to normal capacity ratio (DA/NC), and according to the EPA,[5] 90% of surface drinking water reservoirs will have higher DA/NC ratios. This issue of CWS watershed characteristics becomes even more relevant in the context of drinking water supplies located along flowing water bodies, where the characteristics of pesticide concentrations are very different than static water supply reservoirs. The use of a high vulnerability static water body to represent pesticide exposure potential in a broad range of both static and flowing water bodies does not capture the variability in these types of drinking water supplies. Second, while the overrepresentation of pesticide use has already been discussed, another related problem is the implicit assumption that all fields in a watershed receive the pesticide application at the same time. This assumption is inappropriate for even the smallest sized watersheds that can support an adequate drinking water supply (such as the 172.8 ha Shipman Reservoir) and has greater invalidity as the size of the CWS watershed increases and the variability of agronomic practices of multiple farms contributes to a broad range in pesticide application dates. Accounting for the variability in application timing when modeling pesticide fate and transport at the watershed scale has been shown to have a significant effect on predicted concentrations in flowing water bodies.[28,29] We have discussed the many factors that are contributing to the unrealistically high estimates of drinking water concentrations of pesticides using the current regulatory modeling approach. Refined approaches to applying the current Tier 2 models, as well as methods for applying alternative models, already exist and have shown promise in their ability to accurately predict pesticide residues in surface water.

These alternative modeling approaches include both newly developed tools as well as models with a longer history. The US EPA is currently working on developing updated modeling tools, such as the Surface Water Calculator (Young, 2013)[30] and the Spatial Aquatic Model,[31] that may be able to address some of the shortcomings of the current modeling approach. The Surface Water Calculator (SWC) is expected to include a replacement to the EXAMS receiving water model called the Variable Volume Water Model (VVWM) which will allow for simulation of dynamic water volumes and a wider range in hydrologic conditions. The Spatial Aquatic Model (SAM) is being designed to simulate both static and flowing water bodies draining a watershed with heterogeneous land use and soils. In addition to US EPA efforts to improve the accepted regulatory modeling tools, several other models reported in the scientific literature have been shown to perform well at the prediction of pesticides in complex watersheds that are typical of surface drinking water systems. The United States Geological Survey Watershed Regressions for Pesticides (WARP) model[32] was designed to predict annual atrazine concentration percentiles in flowing water bodies across the US. The WARP model was shown by both Jones[19] and Jackson et al.[22] to predict pesticide concentrations closer to monitoring data than the standard Index Reservoir modeling method. The WARP model was originally developed based on a statistical analysis of atrazine monitoring data and has since been adopted for use with other pesticides through incorporation of a surface water mobility index.[33] The strength of the WARP model is that it was built on robust monitoring data sets; however, because it is not physically based, it is unable to provide important functions such as the simulation of alternative Best Management Practices. This model also has limited testing on pesticides for target crops with a smaller geographic extent than corn.

Promising opportunities for developing a modeling approach that addresses the shortcomings in the current regulatory modeling method reside in the application of exiting watershed scale models that have a proven ability to accurately represent the hydrochemical processes that are necessary for pesticide fate and transport prediction. These tools could easily work into the current regulatory process as a higher tier refinement and could be utilized to simulate either additional representative scenarios or individual drinking water−watersheds of specific concern. One of the most widely used watershed scale models is the Soil and Water Assessment Tool (SWAT) developed and maintained by the United States Department of Agriculture.[34] SWAT is a watershed-scale, continuous, physically based, semidistributed model that has been used in a broad range of hydrologic and water quality applications.[35] One of SWAT's strengths is its ability to simulate the water quality impact of alternative management practices, including tillage practices, buffers and grassed waterways, and pesticide application practices. The use of the SWAT model in the simulation of pesticide transport at the watershed scale has been reported in the literature since at least 2005, and SWAT was recently selected from a pool of 36 models as one of the most appropriate for watershed-scale simulation of pesticides.[36] Pesticide transport modeling with SWAT has included assessments of pesticides in both static and flowing water bodies. Winchell et al.[28] and Peranginangin et al.[37] developed and evaluated a SWAT modeling methodology which focused on identifying a parametrization approach that takes advantage of intelligent use of data in place of extensive site-specific calibration for use in aquatic pesticide concentration predictions in complex watersheds. Another watershed-scale modeling approach based on the PRZM model is the PRZM-Hybrid modeling method described by Snyder et al.[38] and in reports by Miller and colleagues.[29,39] The PRZM-Hybrid approach utilizes spatially explicit high-resolution NEXRAD radar rainfall data, additional meteorology data, field-scale soil properties from the US national SSURGO database, and spatially explicit land use data as input data to model daily watershed runoff concentrations. Both the SWAT and PRZM-Hybrid models are designed for simulation of complex, spatially heterogeneous watersheds and could be readily adapted to serve the purposes of modeling EDWCs for the purposes of human exposure risk assessments. In order for either of these models to generate accurate pesticide concentration predictions when compared to monitoring data, a good understanding of pesticide use information needs to be incorporated. If used in a regulatory context, the models have the ability to represent more complex and realistic hydrology, soil, weather, and application technologies than is possible with the models currently used by EPA. USEPA scientists and pesticide registrants have evaluated the use of watershed modeling

approaches in the past,[40] and because many of the tools have matured, a similar effort should be explored again.

Regardless of the model platform, achieving more realistic model predictions of EDWCs will require incorporating accurate assumptions on pesticide use intensity (i.e., pounds of pesticide per acre of watershed) into the regulatory modeling framework. The current assumption that any pesticide evaluated is applied to 100% of the maximum possible extent defined by its label is overly conservative for even the most widely used pesticides. This implausible assumption is the driving factor leading to the common occurrence of 3 to 5 orders of magnitude model overpredictions of EDWCs that were shown in Figure 2. Strong evidence to support the incorporation of realistic pesticide use assumptions in watershed scale modeling is found in recent studies where WARP (which explicitly accounts for pesticide use intensity) was shown to much more closely match monitoring data than the current regulatory modeling approach.[19,22] Information and techniques similar to those used by the USGS in their recently released national pesticide use maps[41] could serve as the foundation for more realistic use estimates but may require additional scale adjustments to be representative of small watersheds.

The data compiled in this paper represents the most complete collection to date of pesticide modeling and monitoring data. The accuracy of the concentration predictions made by the current regulatory modeling approach was shown to be poor, with significant overprediction common. Some of the primary reasons for this overprediction were discussed, including the regulatory modeling assumptions of pesticide use, a lack of application timing variability, reservoir and watershed geometry, and missing spatial heterogeneity of the watershed. In order for many of these shortcomings to be addressed, a watershed scale modeling approach will need to be adopted and databases of more accurate pesticide use information will need to be compiled. Several existing watershed modeling approaches were proposed, each of which has already shown promise in predicting pesticide concentrations in watersheds of similar size and complexity to typical CWS watersheds. A suggested next step is to take a closer look at several of the watershed scale models introduced in this discussion and determine which ones best fit the needs of regulatory modeling and result in more accurate predictions of EDWCs.

AUTHOR INFORMATION

Corresponding Author

*Phone: 802-229-1882. Fax: 802-229-5417. E-mail: mwinchell@stone-env.com.

Notes

The authors declare no competing financial interest.

REFERENCES

(1) USEPA. 2007, About Water Models—Water Exposure Models Used by the Office of Pesticide Programs, Available at http://www.epa.gov/oppefed1/models/water/models4.htm (Accessed November 20, 2013).

(2) Suarez, L. A. *PRZM-3, A Model for Predicting Pesticide and Nitrogen Fate in Crop Root and Unsaturated Zones: Users Manual for Release 3.12.3*; EPA/600/R-05/111 (NTIS PB2006-101105); National Exposure Research Laboratory, U.S. Environmental Protection Agency: Washington, DC, 2005; p 426.

(3) Burns, L. *Selected water supply reservoirs and finished drinking water 1999–2000: Summary of results from a pilot monitoring program*; United States Environmental Protection Agency: Sacramento, CA, 2004; Publication 01-456.

(4) ECOFRAM. ECOFRAM Aquatic Report, Ecological Committee on FIFRA Risk Assessment Methods (ECOFRAM). US Environmental Protection Agency: Washington, DC, 1999.

(5) Jones, R. D.; Abel, S.; Effland, W.; Matzner, R.; Parker, R. An Index Reservoir for Use in Assessing Drinking Water Exposure. Chapter IV in Proposed Methods for Basin Scale Estimation of Pesticide Concentrations in Flowing Water and Reservoirs for Tolerance Reassessment. Presentation given at the FIFRA Science Advisory Panel; Washington, DC, 1998.

(6) Jones, R. D.; Costello, K.; Hetrick, J. A.; Parker, R. D.; Thurman, N.; Peck, C. *Development and Use of the Index Reservoir in Drinking Water Exposure Assessments*; Office of Pesticide Programs, Environmental Protection Agency: Washington, DC, 2010.

(7) Echeverria, M.; Jones, R. D.; Peck, C.; Ruhman, M.; Shelby, A.; Thawley, S.; Thurman, N. *Development and Use of Percent Cropped Area and Percent Turf Area Adjustment Factors in Drinking Water Exposure Assessments: 2012 Update*; Office of Pesticide Programs, US Environmental Protection Agency: Washington, DC, 2012.

(8) OPP. 2010. *Development and Use of Percent Cropped Area Adjustment Factors in Drinking Water Exposure Assessments. Environmental Fate and Effects Division. September 9, 2010.*

(9) Dubus, I. G.; Brown, C. D.; Beulke, S. Sources of uncertainty in pesticide fate modeling. In *Pesticide Behavior in Soils and Water: BCPC Symposium Proceedings No. 78*; British Crop Protection Council: Farnham, UK, 2001; pp 239–244.

(10) Havens, P. L.; Carbone, J. P.; Warren-Hicks, W.; Fouch, M. A. Development of a Monte Carlo sampling shell for the pesticide root zone model and its application by the Federal Insecticide, Fungicide, and Rodenticide Act Environmental Modeling Validation Task Force. *Environ. Toxicol. Chem.* **2002**, *21*, 1566–1569.

(11) Carbone, J. P.; Havens, P. L.; Warren-Hicks, W. Validation of pesticide root zone model 3.12: Employing uncertainty analysis. *Environ. Toxicol. Chem.* **2002**, *21*, 1578–1590.

(12) Cryer, S. A.; Applequist, G. E. Direct treatment of uncertainty. Part II—Applications in pesticide runoff, leaching and spray drift exposure modeling. *Environ. Eng. Sci.* **2003**, *20*, 169–181.

(13) Harmel, R. D.; Smith, P. K. Consideration of Measurement Uncertainty in the Evaluation of Goodness-of-fit in Hydrologic and Water Quality Modeling. *J. Hydrol.* **2007**, *337*, 326–336.

(14) Harmel, R. D.; Smith, D. R.; King, K. W.; Slade, R. M. Estimating storm discharge and water quality data uncertainty: A software tool for monitoring and modeling applications. *Environ. Model. Software* **2009**, *24*, 832–842.

(15) Crawford, C. G. Sampling strategies for estimating acute and chronic exposures of pesticides in streams. *J. Am. Water Resour. Assoc.* **2004**, *40*, 485.

(16) Mosquin, P.; Whitmore, R. W.; Chen, W. Estimation of Upper Centile Concentrations Using Historical Atrazine Monitoring Data from Community Water Systems. *J. Environ. Qual.* **2012**, *41*, 834.

(17) Hetrick, J. A. Development and Use of Bias Factors. Presentation given at the CLA and Rise Spring Conference, Crystal City, CA, 2013.

(18) Chen, W.; Mosquin, P.; Truman, C. C. Sampling Bias Factors: Compensation for "Missing the Peak. Presentation given at the CLA and Rise Spring Conference. Crystal City, CA, 2013.

(19) Jones, R. L. Comparison of regulatory estimates of drinking water concentrations with monitoring data. *J. Agric. Food Chem.* **2005**, *53*, 8835–9.

(20) Jackson, S.; Hendley, P.; Jones, R.; Poletika, N.; Russell, M. Comparison of regulatory method estimated drinking water exposure concentrations with monitoring results from surface drinking water supplies. *J. Agric. Food Chem.* **2005**, *53*, 8840–8847.

(21) Hertl, P.; Gustafson, D. I.; Jackson, S. H.; Jones, R. L.; Russell, M. H.; Schocken, M. J. A Comparison of US EPA's Tier 1 and 2 Index Reservoir Model Estimates to Drinking Water Reservoir Monitoring Results in Selected US Systems in 1999/2000. Poster 5c.05 presented

at the 10th International Congress Pesticide Chemistry, Basel, August 2002. In *Book of Abstracts*; Basel, Switzerland, 2002; Vol. 2, p 125.

(22) Jackson, S. H.; Jones, J. J.; Hanzas, J. Comparison of Regulatory Method Estimated Drinking Water Exposure Concentrations with Monitoring Results from Surface Water Drinking Supplies. In *Pesticide Exposure Assessment and Predictive Modeling Tools*; ACS Symposium Series; American Chemical Society: Washington, DC, 2010; Vol. *1028*, pp 71−95.

(23) Nandihalli, U. B.; Jones, R. L.; Allen, R.; Ramanarayanan, T. S.; Sabbagh, G. J. Surface Drinking Water Assessment and Monitoring for Oxadiazon Herbicide on Golf Courses. In *Turf Grass: Pesticide Exposure Assessment and Predictive Modeling Tools*; ACS Symposium Series; 2010; pp 57−69.

(24) Jones, R. D. Measuring and Estimating Concentrations of Pesticides in Drinking Water: A Historical Perspective. Presentation given at the EPA Exposure Modeling Public Meeting; Washington, DC, 2012.

(25) Blomquist, J. D.; Denis, J. M.; Cowles, J. L.; Hetrick, J. A.; Jones, R. D.; Birchfield, N. B. *Pesticides in selected water-supply reservoirs and finished drinking water, 1999−2000: Summary of results from a pilot monitoring program*; Publication 01-456; U.S. Dept. of the Interior, U.S. Geological Survey: Baltimore, MD, 2001; p 65.

(26) Grube, A.; Donaldon, D.; Kiely, T.; Wu, L. *Pesticides Industry Sales and Usage: 2006 and 2007 Market Estimates*; Biological and Economic Analysis Division, Office of Pesticide Programs, Office of Chemical Safety and Pollution Prevention, U.S. Environmental Protection Agency: Washington, DC, 2011.

(27) United States Department of Agriculture (USDA). *Conservation Buffers to Reduce Pesticide Losses*; USDA Natural Resources Conservation Service: Washington, DC, 2000; p 21.

(28) Winchell, M.; Peranginangin, N.; Srinivasan, R. A Comparison of SWAT Pesticide Simulations Based on Different Input Resolutions Using a Minimal Calibration Approach. Presentation at the International SWAT Conference, Toledo, Spain, 2011.

(29) Miller, P. S.; Northcott, W. J.; Andrus, J. M.; Harbourt, C. M.; Hendley, P. *PRZM-Hybrid Modeling System Utilizing an Agronomic Approach to Define Watershed Scale Chemical Applications*; Syngenta Task No. TK0023394; Syngenta: Wilmington, DE, 2012.

(30) Young, D. F. Surface Water Calculator. Presentation given at the EPA Exposure Modeling Public Meeting; Washington, DC, 2013.

(31) Thurman, N. Spatial Aquatic Model (SAM) Pilot Project. Presentation given at the EPA Exposure Modeling Public Meeting; Washington, DC, 2013.

(32) Larson, S. J.; Crawford, C. G.; Gilliom, R. J., Development and application of Watershed Regressions for Pesticides (WARP) for estimating atrazine concentration distributions in streams; *U.S. Geological Survey Water-Resources Investigations Report 03-4047*; 2004; p 68.

(33) Chen, W.; Hertl, P.; Chen, S.; Tierney, D. P. A pesticide surface water mobility index and its relationship with concentrations in agricultural drainage watersheds. *Environ. Toxicol. Chem.* **2002**, *21*, 298−308.

(34) Arnold, J. G.; Srinivasan, R.; Muttiah, R. S.; Williams, J. R. Large-area hydrologic modeling and assessment. Part I. Model development. *J. Am. Water Resour. Assoc.* **1998**, *34*, 73−89.

(35) Gassman, P. W.; Reyes, M. R.; Green, C. H.; Arnold, J. G. The Soil and Water Assessment Tool: Historical development, applications, and future research directions. *Trans. ASABE* **2007**, *50*, 1211−1240.

(36) Quilbe, R.; Rousseau, P.; Lafrance, P.; Leclerc, J.; Amrani, M. Selecting a Pesticide Fate Model at the Watershed Scale Using a Multicriteria Analysis. *Water Qual. Res. J. Canada* **2006**, *41*, 283−295.

(37) Peranginangin, N.; Winchell, M.; Folle, S. Evaluation of a Simplified SWAT Model Approach for Prediction of Insecticide Concentrations in a Small Watershed in Northwestern Oregon. Presentation given at the 244th ACS National Meeting & Exposition; American Chemical Society: Philadelphia, PA, 2012.

(38) Snyder, N. J.; Harbourt, C. M.; Miller, P. S.; Trask, J. R.; Hendley, P.; Johnston, E. A. *Analysis of Chemograph Behavior Between Grab Samples - Measurement and Hybrid PRZM Approaches*; Syngenta Task No. T001508-03; Syngenta: Wilmington, DE, 2007.

(39) Miller, P. S.; Northcott, W. J.; Andrus, J. M.; Zwilling, L. F.; Cheplick, J. M.; Harbourt, C. M.; Hendley, P. *Development of the PRZM-Hybrid Watershed Exposure Modeling System Methodology Report*; Syngenta Task No. TK0023394; Syngenta: Wilmington, DE, 2011.

(40) Parker, R.; Arnold, J. G.; Barrett, M.; Burns, L.; Carrubba, L.; Neitsch, S. L.; Snyder, N. J.; Srinivasan, R. Evaluation of Three Watershed-Scale Pesticide Environmental Transport and Fate Models. *J. Am. Water Resour. Assoc.* **2007**, *43*, 1424−1443.

(41) Stone, W. W. *Estimated annual agricultural pesticide use for counties of the conterminous United States, 1992−2009*; U.S. Geological Survey Data Series 752; Pamphlet; United States Geological Survey: Washington, DC, 2013; p 1.